

WHAT IS CLAIMED IS

1. An epoxy resin composition comprising :
 - 5 (a) an epoxy compound which has two or more epoxy groups per molecule,
 - (b) a polythiol compound which has two or more thiol groups per molecule,
 - (c) a latent hardener, and
 - 10 (d) at least one solid organic acid which is substantially insoluble in a mixture of (a), (b) and (c) above, at room temperature.
2. An epoxy resin composition comprising :
 - 15 (a) an epoxy compound which has two or more epoxy groups per molecule,
 - (b) a polythiol compound which has two or more thiol groups per molecule,
 - 20 (c) a latent hardener, and
 - (d) at least one solid organic acid selected from the group consisting of : aliphatic, cycloaliphatic and aromatic carboxylic acids and derivatives thereof, aliphatic, cycloaliphatic and aromatic quinones and derivatives thereof, phenols and
25 derivatives thereof and enolisable aliphatic, cycloaliphatic and aromatic compounds and derivatives thereof.
3. An epoxy resin composition comprising :
 - 30 (a) an epoxy compound which has two or more epoxy groups per molecule,
 - (b) a polythiol compound which has two or more thiol groups per molecule,

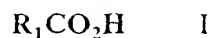
(c) a latent hardener, and

(d) at least one solid organic acid having a pKa of less than or equal to about 12.0,
 5 desirably less than or equal to about 10, more suitably less than or equal to about 9.0, and desirably less than or equal to about 7.5.

4. An epoxy resin according to claim 2 or claim 3 wherein the acid (d) is substantially insoluble in a mixture of (a), (b) and (c), at room temperature.

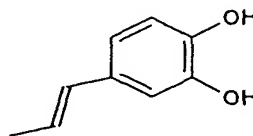
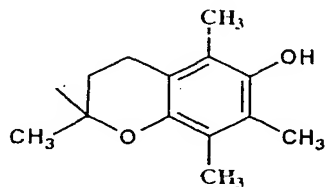
10 5. An epoxy resin composition as claimed in any preceding claim wherein the organic acid selected is from :-

(i) carboxylic acids of general Formula I

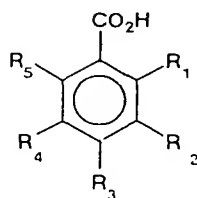


wherein :

20 R_1 is trans-CH=CHCO₂H, -CH=CHCO₂R [R is CH₃],
 -CH₂C(OR')(CO₂R'')CH₂CO₂R''',
 [R' is H, C₁-C₁₀alkyl, Ar], [R'' is H, C₁-C₁₀alkyl, Ar], [R''' is H, C₁-C₁₀alkyl, Ar], C₁₁-
 C₁₈ alkyl, -(CH₂)_nCO₂H [n is 1-9], -(CHR)_nCO₂H [R is H, OH, n is 1 or 2],
 -CH(OR')R'' [R' is H, alkyl, R''=C₁-C₁₀ alkyl, Ph], -CH=CH-Ar,



(ii) benzoic acids of general Formula II :



wherein :

R_1 is H, alkyl, haloalkyl such as CX_3 [X is F, Cl, Br, I], alkenyl, OH, OR [R is alkyl, Ph,

Bn, Ar], -S-S-Ar- CO_2H , -S-S-Ar;

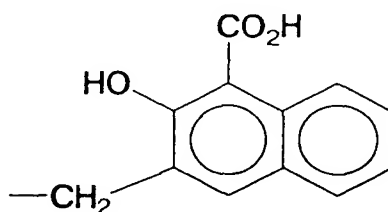
-SR [R is H, alkyl, haloalkyl, Ph, Bn, Ar], Ph, Bn, Ar, CO_2R [R is H, alkyl, Ph, Bn, Ar],

$CO.R$ [R is H, alkyl, Ph, Bn, Ar], NO_2

R_2 is H, alkyl, haloalkyl such as CX_3 [X is F, Cl, Br, I], alkenyl,

Ph, Bn, Ar, OH, OR, [R is alkyl, Ph, Bn, Ar], $-CH_2Ar$, NO_2 , $CO.R$ [R is C_1-C_{10} -

alkyl, Ph, Bn, Ar], CHO, CO_2R [R is H, alkyl, haloalkyl, Ph, Bn, Ar], or



R_3 is H, alkyl, haloalkyl such as CX_3 [X is F, Cl, Br, I], alkenyl, OH, OR [R is alkyl, Ph,

Bn, Ar] Ph, Bn, Ar, alkyl, CHO, $CO.R$ [R is alkyl, Ph, Bn, Ar], CO_2R [R is H, alkyl, Ph,

Bn, Ar] NO_2 ;

R_4 is H, alkyl, haloalkyl such as CX_3 [X is F, Cl, Br, I], alkenyl, OH, OR [R is alkyl, Ph, Bn, Ar], NO_2 , $CO.R$ [R is alkyl, Ph, Bn, Ar], CHO, CO_2R [R is H, alkyl, Ph, Bn, Ar], Ph, Bn, Ar;

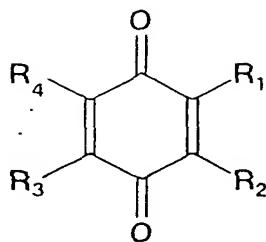
- 5 R_5 is H, alkyl, haloalkyl such as CX_3 [X is F, Cl, Br, I], alkenyl, OH, OR [R is alkyl, Ph, Bn, Ar], Ph, Bn, Ar, CHO, $CO.R$ [R is alkyl, Ph, Bn, Ar], CO_2R [R is H, alkyl, Ph, Bn, Ar], NO_2 ,

or

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(iii) quinones of general Formula III:

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wherein :

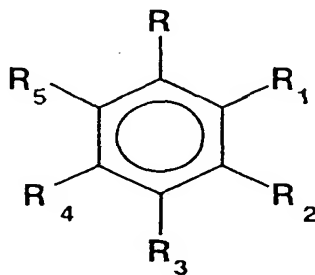
R_1 , R_2 , R_3 and R_4 are independently H, alkyl, haloalkyl, alkenyl, OR [R is H, alkyl, Ar, Ph, Bn,]CN, Ph, Ar, or

25

(iv) phenols of general Formula IV :

30

wherein :



R is H, OH;

R₁ is H, alkyl, haloalkyl such as CX₃[X is F, Br, Cl, I], alkenyl,

Cl, F, Br, I, CN, OH, OR[R is alkyl, Ph, Bn, Ar], NO₂, CO.R[R is alkyl, Ph, Bn, Ar],

5 CHO, CO₂R[R is H, alkyl, Ph, Bn, Ar], PhOH,

R₂ is H, alkyl, haloalkyl, alkenyl, OH, OR[R is alkyl, Ph, Bn, Ar],

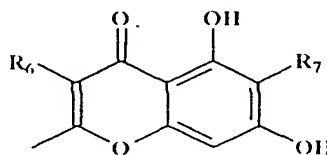
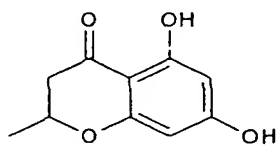
Ph, Bn, -CH₂Ar, CN, F, Cl, Br, I,

10 R₃ is H, alkyl, haloalkyl such as CX₃[X is F, Br, Cl, I], alkenyl, NO₂,

CO.R[R is alkyl, Ph, Bn, Ar], CHO, CO₂R[R is alkyl, Ph, Bn, Ar],

OH, OR[R is alkyl, Ph, Bn, Ar], Ar, Bn, Ph,

C(R)₂PhOH[R is Me or H], C(R)₂Ar[R is Me or H] or:



15 wherein :

R₆ and R₇ are independently H, alkyl, haloalkyl, alkenyl, OH, OR
[R is alkyl, Ph, Bn, Ar];

20 R₄ is H, alkyl, haloalkyl, alkenyl, OH, OR[R is alkyl, Ph, Bn, Ar], F, Cl, Br, I, CN, Ph,
Bn, -CH₂Ar;

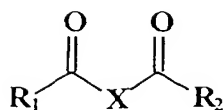
R₅ is H, alkyl, haloalkyl such as CX₃[X is F, Br, Cl, I], alkenyl,

F, Cl, Br, I, CN, OH, OR[R is alkyl, Ph, Bn, Ar], NO₂, CO.R

[R is alkyl, Ph, Bn, Ar], CHO, CO₂R[R is H, alkyl, Ph, Bn, Ar], PhOH,

25 provided that a compound of general Formula V is chosen to have at least one phenolic
group present, or

(v) enolisable materials of general Formula IV:



5 wherein :

R_1 or R_2 are $\text{NR}'\text{CO.NR}''\text{R}'''$ [R' is H, alkyl, Ph, Ar, R'' is H, alkyl, Ph, Ar

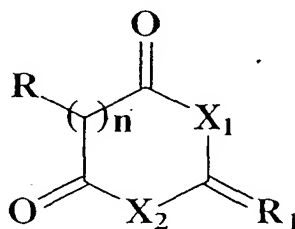
R''' is H, alkyl, Ph, Ar,], OR [R is H, alkyl, Ph, Ar]

X is $(\text{CH}_2)_n$, $\text{C}(\text{R})_2$ [R is alkyl, Ph, Ar, CN], O, S, NR [R is H, alkyl, Ph, Ar], n is 0-10,

10 or

(vi) enolisable materials of general Formula VI:

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wherein

(a) $\text{X}_1=\text{X}_2=\text{NH}$, $\text{R}=\text{H}$, $\text{R}_1=\text{O}$, $n=1$; or

(b) $\text{X}_1=\text{X}_2=\text{NH}$, $\text{R}_1=\text{O}$, n is zero so that the cyclic structure has a five membered
25 ring; or

(c) $\text{X}_1=\text{X}_2=\text{O}$, $\text{R}=\text{H}$, $\text{R}_1=(\text{CH}_3)_2$, $n=1$; or

(d) $\text{X}_1=\text{X}_2=\text{O}$, $\text{R}=\text{Ph}$, $\text{R}_1=(\text{CH}_3)_2$, $n=1$.

6. An epoxy resin composition as claimed in any preceding claim wherein the solid organic acid is selected from the group consisting of :
 4-Nitroguaiacol, 3,4,5-Trimethoxy benzoic acid, Hexachlorophene, 3,5-Dinitrosalicylic acid, 4,5,7-Trihydroxyflavanone, 2,2-Dithiosalicylic acid, Phloroglucinol, Fumaric acid, 3,4-Dihydroxy benzoic acid, 3,4,5-Trihydroxy benzoic acid, 6-hydroxy-2,5,7,8-tetramethylchroman-2 carboxylic acid, Pamoic acid, Ascorbic acid, Salicylic acid, Citric acid, 3,4-Dihydroxy cinnamic acid, 2,3-Dicyanohydroquinone, Barbituric acid, Tetrahydroxy-p-benzoquinone, Parabanic acid, Phenyl boronic acid, 5-Phenyl Meldrum's acid and Meldrum's acid.

7. An epoxy resin composition as claimed in any preceding claim wherein the epoxy compound is selected from any polymeric epoxide which has an average of two or more epoxide groups per molecule, including polyglycidyl ethers of bisphenol A, bisphenol F, bisphenol AD, catechol, resorcinol, or epoxy compounds obtained by reacting polyhydric alcohols such as butanediol or polyethylene glycol with epichlorohydrin, epoxidised olefinic resins, phenolic novolac resins, cresol novolac resins, cycloaliphatic epoxy resins, glycidyl ether esters, polyglycidyl esters, urethane modified esters and polyepoxy compounds based on aromatic amines and epichlorohydrin.

8. An epoxy resin composition as claimed in any preceding claim wherein the polythiol compound is selected from any mercapto compound which has two or more thiol groups per molecule such as trimethylolpropane tris (β-mercaptopropionate), trimethylolpropane tris (thioglycolate), pentaerythritol tetrakis (thioglycolate), pentaerythritol tetrakis (β-mercaptopropionate), dipentaerythritol poly (β-mercaptopropionate), ethylene glycol bis (β-mercaptopropionate) and alkyl polythiols such as butane-1,4-dithiol, hexane-1,6-dithiol, and aromatic polythiols such as p-xylenedithiol and 1,3,5-tris (mercaptomethyl) benzene.

9. An epoxy resin composition as claimed in any preceding claim wherein the ratio of the epoxy compound to the polythiol compound in the composition is such that the

ratio of epoxy equivalents to thiol equivalents is from about 0.5:1 to about 1.5:1, more suitably about 0.75:1 to about 1.3:1.

10. An epoxy resin composition according to any preceding claim wherein the latent
5 hardener (c) is present in amounts of about 1 to about 60 parts by weight per 100 parts by weight of the epoxy compound (a), suitably about 1 to about 45 parts more suitably about 1 to about 30, desirably about 10 to about 20, parts by weight.

11. An epoxy resin composition according to any preceding claim wherein the solid
10 organic acid is present in an amount of about 0.1 to about 80 parts by weight per 100 parts by weight of the latent hardener (c), suitably about 0.5 to about 45 parts by weight, desirably about 1 to about 5 parts by weight.

12. An epoxy resin composition according to any preceding claim wherein the acid
15 has a mean particle size in the range about 0.1 to about 500 microns, suitably about 5 to about 100 microns, and desirably about 10 to about 50 microns.

13. An epoxy resin composition according to any preceding claim comprising two
20 or more solid organic acids.

14. An epoxy resin composition according to any preceding claim wherein the
composition is a one-part adhesive composition.

15. An epoxy resin composition according to any preceding claim wherein the
25 composition further comprises:

(e) a thixotropy-conferring component.

16. A curable one-part epoxy resin composition with improved rheological
properties suitable for use as an adhesive to mount electronic components on a
30 substrate, the one-part composition comprising the components of a composition according to any preceding claim.

17. A curable one-part epoxy composition capable of sealing underfilling between a semiconductor device including a semiconductor chip mounted on a carrier substrate and a circuit board to which said semiconductor device is electrically connected, said one-part composition comprising the components of a composition according to any preceding claim.
18. A composition according to claim 15 having yield point maintenance and viscosity maintenance over time.
19. A curable one-part epoxy resin composition with improved rheological properties, comprising:
- (i) an epoxy component comprising at least one epoxy compound,
 - (ii) a latent hardener component, and
 - (iii) a thixotropy-conferring component, and
 - (iv) a solid organic acid component,
- wherein the solid organic acid component improves the yield point maintenance and viscosity maintenance of the composition over time.
20. A curable one-part epoxy resin composition with improved rheological properties suitable for use as an adhesive to mount electronic components, comprising:
- (i) an epoxy component comprising at least one epoxy compound,
 - (ii) a latent hardener component,
 - (iii) a thixotropy-conferring component, and
 - (iv) a solid organic acid component,
- wherein the solid organic acid component improves the yield point maintenance and viscosity maintenance of the composition over time.
21. A curable one-part epoxy resin composition with improved rheological properties suitable for use as an adhesive to mount electronic components, comprising:
- (i) about 150 parts of an epoxy component comprising at least one epoxy compound,
 - (ii) about 42.36 parts of a latent hardener component,

- (iii) about 19.26 parts of a thixotropy-conferring component, and
- (iv) about 1 part of a solid organic acid component.

22. A curable one-part epoxy resin composition with improved rheological
5 properties suitable for use as an adhesive to mount electronic components, comprising:
 (i) about 171.67 parts of an epoxy component comprising at least one epoxy
 compound.
 (ii) about 42.36 parts of a latent hardener component.
 (iii) about 19.26 parts of a thixotropy-conferring component, and
10 (iv) about 1 part of a solid organic acid component.
23. A curable one-part epoxy resin composition with improved rheological
properties suitable for use as an adhesive to mount electronic components, comprising:
 (a) about 100 parts of an epoxy component comprising at least one epoxy
15 compound,
 (b) about 25 parts of a latent hardener component,
 (c) about 15.6 parts of a thixotropy-conferring component,
 (d) about 75 part of a polythiol component, and
 (e) about 0.5 parts of a solid organic acid component
20
24. A curable one-part epoxy resin composition with improved rheological
properties suitable for use as an adhesive to mount electronic components, comprising:
 (a) about 130.26 parts of an epoxy component comprising at least one epoxy
 compound,
25 (b) about 33.26 parts of a latent hardener component,
 (c) about 20.57 parts of a thixotropy-conferring component,
 (d) about 94.5 parts of a polythiol component, and
 (e) about 0.635 parts of solid organic acid component.
- 30 25. A curable one-part epoxy resin composition with improved rheological
properties suitable for use as an adhesive to mount electronic components, comprising:
 (a) an epoxy component comprising at least one epoxy compound,

(b) a latent hardener component, and

(c) a thixotropy-conferring component, and

(d) a solid organic acid component, wherein the composition has a yield point in the range of about 30-700 Pa, suitably about 150 - 450 Pa, desirably about 300-400 Pa, and a viscosity in the range of about 1 to 50 Pa.s, suitably about 1 to 25 Pa.s, desirably about 1 to 10 Pa.s, more desirably about 3-4 Pa.s, with each of which being maintained substantially within the respective ranges over time.

26. A process for preparing curable one-part epoxy resin composition with improved rheological properties, comprising the steps of:

combining initially (i) an epoxy component comprising at least one epoxy component, (iii) a thixotropy-conferring component, and (iv) a solid organic acid component,

combining thereafter (ii) a latent hardener component, and

mixing together components (i), (ii), (iii) and (iv) for a time sufficient to form the curable one-part epoxy composition with improved yield point maintenance and viscosity maintenance.

27. A mounting structure for semiconductor devices; comprising:
a semi conductor device comprising a semiconductor chip mounted on a carrier substrate; and a circuit board to which the semi-conductor device is electrically connected, wherein the space between the carrier substrate of the circuit board and the semi-conductor device is sealed with the cure product of a composition according to any of claims 1 to 25.

28. An electronic device comprising a semiconductor device and a circuit board to which said semiconductor device is electrically connected, assembled using an epoxy resin composition according to any of claims 1 to 25 to mount the semiconductor device to the circuit board.

29. A method of using a composition according to any claims 1 to 25, the method comprising the steps of:

dispensing onto an appropriate location on a carrier substrate a sufficient amount of the composition,

positioning over the location bearing the composition an electronic component,

5 mating the electronic component with the carrier substrate, and

exposing the mated electronic component/carrier substrate assembly to conditions favourable to effect cure of the composition.

30. A method of underfilling a space between an electronic component and a
10 carrier substrate the electronic component being mounted on the carrier substrate, comprising the step of dispensing an amount of a composition according to any one of claims 1 to 25 into the space between the electronic component and the carrier substrate, and exposing the epoxy resin composition to conditions which effect cure.

15 31. Use of at least one solid organic acid having a pK_a of less than or equal to about 12.0, suitably less than or equal to about 10.0, more suitably less than or equal to about 9.0, and desirably less than or equal to about 7.5, in the preparation of one-part adhesive composition based on an epoxy resin.

20 32. The reaction product of a composition according to any one of claims 1 to 25.